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Recovery of Fluorite and Byproducts From Fish Creek Deposit, Eureka County, NV

By F. W. Benn, D. G. Foot, Jr., and J. L. Huiatt

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	min	minute
lb	pound	pct	percent
lb/st	pound per (short) ton	st	short ton (U.S.)
µm	micrometer	wt pct	weight percent

RECOVERY OF FLUORITE AND BYPRODUCTS FROM FISH CREEK DEPOSIT, EUREKA COUNTY, NV

By F. W. Benn,[1] D. G. Foot, Jr.,[2] and J. L. Huiatt[3]

ABSTRACT

The Bureau of Mines investigated flotation methods for recovering fluorite and byproducts from two samples of the Fish Creek deposit in Eureka County, NV. The preferred method for treating a fluorite-beryllium sample included (1) fluorite rougher and cleaner flotation, (2) desliming at 20 μm, (3) muscovite flotation, (4) silicate flotation, (5) sodium hypochlorite wash of silicate concentrate, and (6) beryllium rougher and cleaner flotation from the silicate concentrate. Laboratory results showed that over 94 pct of the fluorite was recovered in a recleaner concentrate containing 98 pct CaF_2. Beryllium flotation produced concentrates containing in excess of 5 pct BeO with recoveries over 70 pct.

The preferred method used for a fluorite-mica sample consisted of (1) fluorite rougher and cleaner flotation, (2) desliming at 20 μm, and (3) mica flotation using an anionic-cationic collector system. Laboratory results showed that 84 pct of the fluorite was recovered in a recleaner concentrate containing 96 pct CaF_2. Mica flotation produced a concentrate containing 95 pct mica at 85-pct recovery.

[1]Minerals engineer.
[2]Group supervisor.
[3]Research supervisor.
Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

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INTRODUCTION

Fluorspar is the commercial name for an aggregate of rock and mineral matter containing a sufficient amount of the mineral fluorite (CaF_2) to qualify as a marketable commodity. Pure fluorite is calcium fluoride, which contains 51.3 pct Ca and 48.7 pct F. Fluorite is the principal source of fluorine, an element for which no adequate substitute has been found. Fluorite is used principally as a fluorine source in the making of (1) hydrofluoric acid (HF), (2) a flux in metallurgy, and (3) a raw material in the manufacture of glass and enamels.

Fluorite is marketed in three grades that have different physical and chemical specifications (1):[4]

Metallurgical grade.--This is also known as "metspar" or "lump spar" and is sold on the basis of effective CaF_2 content rather than the actual CaF_2 content. The effective CaF_2 content is derived by subtracting 2.5 times the percentage of the silica (SiO_2) content from the percentage of CaF_2 content. "Metspar" users require 60 to 70 pct effective CaF_2, limit SiO_2 to 5 or 6 pct, limit sulfides to under 0.50 pct, and limit lead to under 0.25 pct. Metallurgical-grade fluorite is used as a flux in steel, as an electrolyte in aluminum smelting, and in metal welding, porcelain enameling, and glazing.

Ceramic grade.--This is also known as "glass" and "enamel" grade and must contain a minimum of 95 pct CaF_2, with a maximum of 2.5 pct SiO_2. It must be fine grained for use in the manufacture of opaque and flint glass, as an ingredient in welding and coatings, in making white- and buff-colored clay bricks, and in vitreous enamels for coating metal articles and appliances.

Acid grade.--This is used in the manufacture of HF and should contain a minimum of 97 pct CaF_2 and not over 1.1 pct SiO_2, 1.25 pct $CaCO_3$, and 0.03 pct S. Acid-grade fluorite is the highest quality marketed and therefore commands the highest price. Major uses include the manufacture of fluorine chemicals, synthetic cryolite (essential for aluminum production), preservatives, insecticides, aerosols, and metal coatings.

Domestic shipments of finished fluorite declined for the third consecutive year in 1984. Fluorite output failed to exceed 100,000 st for only the fourth time since 1938. Mexico remained the major supplier of metallurgical- and acid-grade fluorite (54 pct), with the Republic of South Africa the second largest supplier (28 pct). Minor amounts were received from China, Italy, Spain, and Kenya (2).

A long-term downward effect on the demand for fluorite and fluorine compounds continues, as steelmakers consume less fluorite per unit of output and primary aluminum smelters adopt and refine technology that recovers and recycles more fluorine. New and expanded uses for fluorine chemicals will offset these decreases in long-term demand. From a 1985 base, consumption of fluorite equivalent is expected to increase at an annual average rate of 2.7 pct through 1990 (2). The long-term U.S. fluorite requirements, of which 91 pct is imported, will have to be derived from secondary sources, submarginal domestic ores, or multicomponent ores (2).

Most domestic fluorite is produced in the Midwest. Production in Illinois accounts for over 90 pct of all U.S. shipments. In the West, production was reported from small mines in Nevada and Texas. Small, unreported amounts of fluorite were produced in Utah, Idaho, and New Mexico (3). Approximately 90 Nevada deposits containing 5 to 50 pct CaF_2, with byproducts of barite, beryllium, scheelite, zinc, gold, and silver, were reported (4-5). Byproduct recovery is necessary to enable economic processing of submarginal domestic reserves.

Traditional methods of concentrating fluorite use gravity separation, followed by flotation. A flotation procedure using oleic acid as a fluorite collector was patented (6) and used to recover acid-grade fluorite from an Illinois jig tailings that contained 44 pct CaF_2. Another procedure, which depressed

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

barite with lignin sulfonate and floated fluorite with oleic acid, was used to beneficiate a Yuma County, AZ, fluorspar ore (7). The Bureau of Mines characterized and devised new flotation beneficiation methods to recover fluorite, muscovite, and beryllium values from the Fish Creek deposit in Nevada. This report summarizes the results of that investigation.

EXPERIMENTAL MATERIALS

Two samples were obtained from the Fish Creek fluorspar deposit near Eureka, NV. One sample was known to contain beryllium values. The samples were crushed and screened through 10 mesh and thoroughly blended, after which representative portions were submitted for chemical and petrographic analysis. The chemical analyses are shown in table 1.

Petrographic analysis of the fluorite-beryllium sample indicated that it contained major amounts of quartz (SiO_2), fluorite (CaF_2), and muscovite (light-colored mica [$KAl_3Si_3O_{10}(OH)_2$]). Minor amounts of hematite (Fe_2O_3), limonite (hydrous iron oxides), sphalerite (ZnS), potassium-feldspar ($KAlSi_3O_8$), beryl ($Be_3Al_2Si_6O_{18}$), calcite ($CaCO_3$), and chlorite (hydrous silicates of aluminum, ferrous iron, and magnesium) were observed. Liberation size was 35 mesh.

TABLE 1. - Chemical analyses of Fish Creek samples, percent

Constituents	Chemical composition	
	Fluorite-beryllium	Fluorite-mica
BeO	0.54	0.03
$CaCO_3$	.8	2.0
CaF_2	10.5	27.1
SiO_2	82.6	54.4
Zn	.3	.2
Total Fe	1.2	1.3
Total mica[1]	4.0	15.0

[1]Estimated by petrography.

Petrographic analyses of the fluorite-mica sample indicated that it contained major amounts of fluorite, quartz, chert (microcrystalline quartz), muscovite, biotite (black mica [$(K,H)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$]), and phlogopite (magnesium mica [$(K,H)_3Mg_3Al(SiO_4)_3$]). Minor amounts of pyrite (FeS_2), hematite, limonite, potassium-feldspar, calcite, serpentine [$Mg_3(SiO_5)(OH)_4$], apatite ($CaFP_3O_{12}$), scheelite ($CaWO_4$), sphalerite, smithsonite ($ZnCO_3$), Willemite (Zn_2SiO_4), franklinite [$(Fe,Mn,Zn)(FeO_2)_2$], an unidentifiable zinc-iron mineral, chlorite, and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) were observed. Liberation size was 35 mesh.

Minus 35-mesh material was prepared for bench-scale testing by stage crushing through a jaw and roll crusher and then pulverizing. Each ore was blended and split into 500-g samples. A screen analysis was performed on the minus 35-mesh samples to determine the distribution of the fluorite and/or beryllium (tables 2 and 3). Only 3.2 pct of both fluorite and beryllium (BeO) values reported to the minus 400-mesh fraction of the fluorite-beryllium sample; about 83 pct of the CaF_2 and BeO reported to the minus 35- plus 400-mesh fraction. Similarly, the minus 400-mesh fraction of the fluorite-mica sample contained 13.7 pct of the fluorite; nearly 73 pct of the fluorite was contained in the minus 35- plus 200-mesh fraction.

TABLE 2. - Screen analysis of fluorite-beryllium sample, percent

Size, mesh	Weight	Analysis		Distribution	
		CaF_2	BeO	CaF_2	BeO
-35, +48	15.4	8.3	0.58	12.2	16.4
-48, +65	18.8	9.7	.61	17.4	21.1
-65, +100	24.0	15.2	.65	34.7	28.8
-100, +200	19.1	10.3	.49	18.7	17.2
-200, +325	10.3	8.6	.43	8.4	8.1
-325, +400	7.5	7.6	.38	5.4	5.2
-400	4.9	6.8	.36	3.2	3.2
Composite	100.0	10.51	.54	100.0	100.0

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TABLE 3. - Screen analysis of fluorite-mica sample, percent

Size, mesh	Weight	CaF_2	
		Analysis	Distribution
-35, +48.....	12.2	29.8	13.4
-48, +65.....	15.0	28.7	15.8
-65, +100.....	17.1	28.9	18.2
-100, +200.....	22.4	30.9	25.7
-200, +325.....	11.5	29.2	12.4
-325, +400.....	.8	28.0	.8
-400.....	21.0	17.7	13.7
Composite.....	100.0	27.1	100.0

EXPERIMENTAL PROCEDURES AND RESULTS

Conventional gravity separation techniques, such as tabling, jigging, and heavy-medium separation, were investigated to concentrate the fluorite. Some upgrading was achieved, but these methods did not produce concentrates of sufficient grades or recoveries. Froth flotation proved to be the most successful. A Denver D-1[5] laboratory flotation machine was used in the flotation testwork.

FLUORITE-BERYLLIUM SAMPLE

Fluorite Flotation

Flotation testing was performed to determine the effects of fluorite rougher flotation of (1) collector addition and conditioning time, (2) flotation pH variation, (3) sodium carbonate (Na_2CO_3) addition and conditioning time, and (4) sodium silicate (Na_2SiO_3) addition and conditioning time. As in the prior procedures (6-7), food-grade oleic acid, a mixture of oleic (72 pct), linoleic, linolenic, and rosin acids, was used as the collector. Tests were conducted varying each factor to determine the optimum, or "preferred," flotation conditions.

The generalized procedure for fluorite flotation consisted of--

1. Pulping ore and water at 50 pct solids.
2. Conditioning with Na_2CO_3.
3. Conditioning with Na_2SiO_3.
4. Adjusting pulp to desired pH level.
5. Conditioning with food-grade oleic acid at desired pH.
6. Rougher flotation for 5 min.

Determination of Preferred Conditions

Collector

Based on tests varying the oleic acid dosage from 0.5 to 3.0 lb/st, a preferred dosage of 2.0 lb/st was determined. In these tests, flotation pH was held at 9.0, and dosage levels were 3 lb/st Na_2CO_3 and 2 lb/st Na_2SiO_3.[6] As shown in figure 1, highest recovery (97 pct of the CaF_2) was at the 2-lb/st addition level. Grade peaked at a slightly lower dosage level; however, in rougher flotation higher recovery is worth a slight tradeoff in grade.

Based on tests varying the oleic acid conditioning time (CT) from 3 to 30 min, a preferred time of 15 min was determined. In these tests, conditioning time was held at 3 min each for Na_2CO_3 and Na_2SiO_3, and dosage levels were held at 3 lb/st for both Na_2CO_3 and Na_2SiO_3 and at 2 lb/st for oleic acid. While recovery showed a continual slight increase (from 95.2 pct at 3 min to 98 pct at 30 min oleic acid CT), grade increased from 65.5 pct CaF_2 at 3 min CT to 72.8 pct at 15 min CT, then fell to 70.4 pct at 30 min CT.

[5]References to specific products does not imply endorsement by the Bureau of Mines.

[6]This was lower than the preferred dosage of 3 lb/st for Na_2SiO_3, which had not yet been determined.

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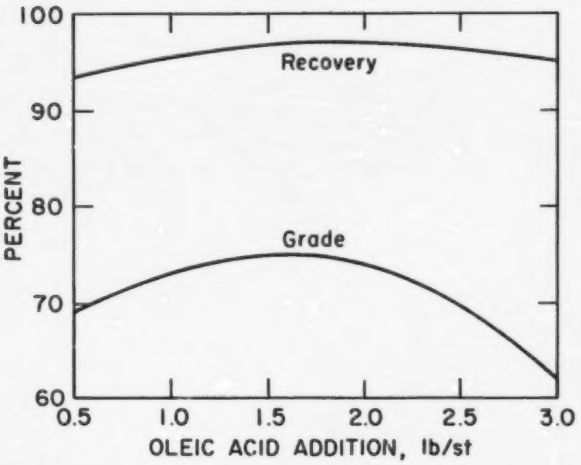

FIGURE 1. - Effect of oleic acid addition on fluorite grade and recovery, fluorite-beryllium sample.

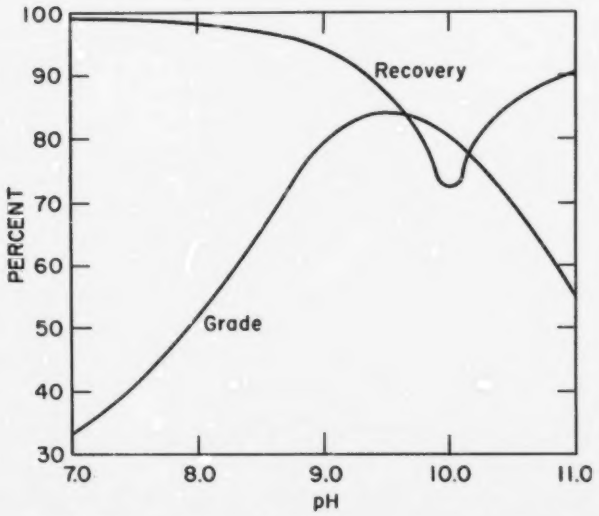

FIGURE 2. - Effect of pH variation on fluorite grade and recovery, fluorite-beryllium sample.

Flotation pH Variation

Prior investigators (8-9) reported that the point-of-zero-charge for fluorite was at pH 10.0; therefore, the pH for fluorite flotation using an anionic collector should theoretically be below pH 10, owing to the positive charge on the fluorite surface. Based on tests using NaOH or HCl to vary pH from 7 to 11, a preferred pH of 9.0 was determined.

In these tests, conditioning times were held at 3 min for each reagent, as preliminary data had indicated that the general effect of pH changed very little with longer times. Reagent dosages were held constant at 3 lb/st Na_2CO_3 and 2 lb/st each for Na_2SiO_3 and oleic acid.[7] As shown in figure 2, maximum grade was achieved at a pH of 9.5, whereas recovery began to fall sharply above pH 9, though rising again above pH 10. At the preferred flotation pH of 9.0, 94.6 pct of the fluorite was recovered in a rougher concentrate of 79.3 pct CaF_2; this pH level was considered the best compromise between grade and recovery.

Sodium Carbonate

Sodium carbonate (Na_2CO_3) was used as a water conditioner and to aid in gangue depression. Based on tests varying dosage levels from 0.5 to 4 lb/st, a preferred dosage of 3 lb/st was determined. In these tests, flotation pH was held at 9.0, CT for all reagents was 3 min, and dosage levels were 2 lb/st for both Na_2SiO_3 and oleic acid. As shown in figure 3, recovery was nearly constant, while maximum grade of 73.2 pct CaF_2 was at 3 lb/st Na_2CO_3, above which level gangue flotation caused a dropoff in grade.

Based on tests varying Na_2CO_3 conditioning time from 3 to 30 min, a preferred time of 15 min was determined. In these tests, CT was held at 3 min each for Na_2SiO_3 and oleic acid, and dosage levels were held at 3 lb/st for Na_2CO_3 and 2 lb/st for both Na_2SiO_3 and oleic acid;[8] flotation pH was 9.0. Recovery held near constant at 97 pct, while grade had slight fluctuation from 78.5 pct CaF_2 at 3 min CT to 82.5 pct CaF_2 at CT's of 15 min and longer.

[7]See footnote 6.
[8]See footnote 6.

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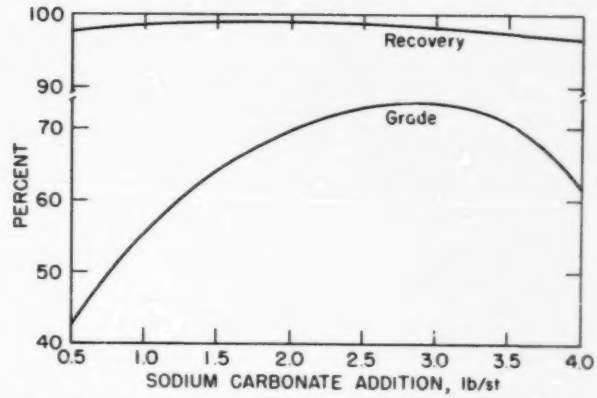

FIGURE 3. - Effect of Na_2CO_3 addition on fluorite grade and recovery, fluorite-beryllium sample.

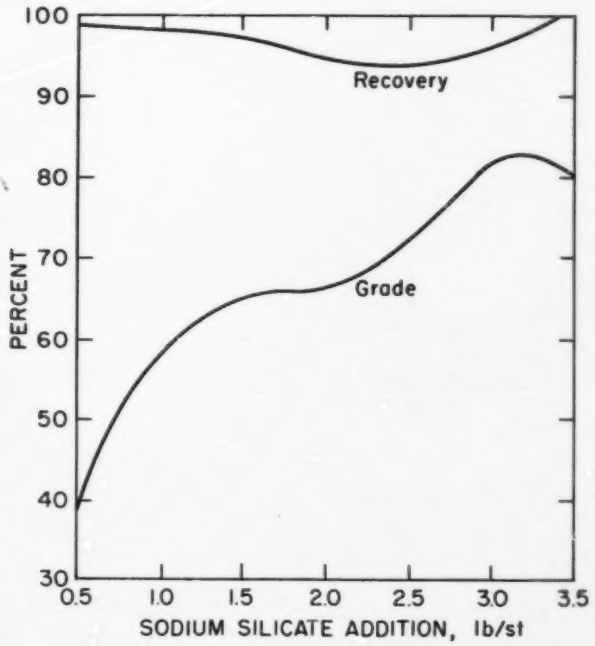

FIGURE 4. - Effect of Na_2SiO_3 addition on fluorite grade and recovery, fluorite-beryllium sample.

Sodium Silicate

Sodium silicate (Na_2SiO_3), with a SiO_2-Na_2O weight ratio of 3.22, was used as a quartz- and silicate-mineral depressant. Based on tests varying dosage levels from 0 to 4 lb/st, a preferred dosage of 3 lb/st was determined. In these tests, flotation pH was 9.0, CT for all reagents was 3 min, and dosage levels were 3 lb/st for Na_2CO_3 and 2 lb/st for oleic acid. As shown in figure 4, recovery dipped slightly between dosage levels of 1.5 and 2.5 lb/st Na_2SiO_3, then increased toward 100 pct above that level. Grade, on the other hand, showed sharp increases up to addition levels of 3 lb/st Na_2SiO_3, then dropped off because of increased gangue flotation.

Based on tests varying Na_2SiO_3 conditioning time from 3 to 30 min, a preferred time of 15 min was determined. In these tests, CT was held at 3 min each for Na_2CO_3 and oleic acid, and dosage levels were held at 3 lb/st for Na_2CO_3 and 2 lb/st for both Na_2SiO_3 and oleic acid;[9] flotation pH was 9.0. Recovery held constant at approximately 95 pct, while grade increased from 65.5 pct CaF_2 at 3 min CT to 80.4 pct at 15 min CT, then dropped to 72 pct at 30 min CT because of increased gangue flotation.

Flotation Under Preferred Conditions

Under preferred conditions--3 lb/st Na_2CO_3, 3 lb/st Na_2SiO_3, and 2 lb/st oleic acid; 15 min CT for each reagent; and flotation pH of 9.0--a fluorite rougher concentrate containing 83 pct CaF_2 was produced with 96.1-pct fluorite recovery. This concentrate was cleaned twice without additional reagents other than those needed to maintain the pH level; the second cleaner concentrate contained 98.1 pct CaF_2 with a recovery of 94 pct.

Locked-Cycle Flotation Testing

Locked-cycle flotation testing was performed to determine the effects of

[9]See footnote 6.

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recycling the cleaner tailings products and recycling water on fluorite flotation. This process was also used to obtain data for scale-up planning. The cleaner tailings and recleaner tailings were combined and scavenged, with the scavenger concentrate being recycled to the head of the next cycle. The fluorite rougher tailings were combined with the scavenger tailings to make the final tailings. Five complete cycles were performed to assure the system was in equilibrium. All water was recycled except the rougher tailings water. Fluorite recovery was 94 pct at a grade of 96 pct CaF_2. The final tailings contained over 90 pct of the weight, with a grade of 0.62 pct CaF_2, representing a loss of 5.78 pct of the fluorite. The concentrate contained 0.01 pct BeO, while the tailings product contained over 99 pct of the BeO values with a grade of 0.60 pct BeO.

Byproduct Recovery

Various procedures were investigated to concentrate the beryl. The preferred method consisted of (1) fluorite flotation using oleic acid, (2) desliming at 20 μm, (3) muscovite flotation using H_2SO_4 and tallow amine acetate, (4) silicate minerals flotation using HF and tallow amine acetate, (5) collector removal from the silicate concentrate using NaOCl, (6) water washing of the silicate concentrate, and (7) beryl flotation from the silicate concentrate using oleic acid (10). The flowsheet is shown in figure 5.

Muscovite Removal

Flotation testing was performed on the muscovite flotation circuit to determine the effect of (1) H_2SO_4 addition and (2) collector (tallow amine acetate) addition. The muscovite had posed a problem in previous testwork because it would concentrate with the beryl, thus lowering the beryl concentrate grade. No reliable analytical method was available for determining muscovite in the flotation products. Preferred conditions were based on (1) the percent BeO values in the muscovite flotation products, (2) the BeO grade of the muscovite tailings, and (3) total weight removed from the deslimed fluorite tailings product.

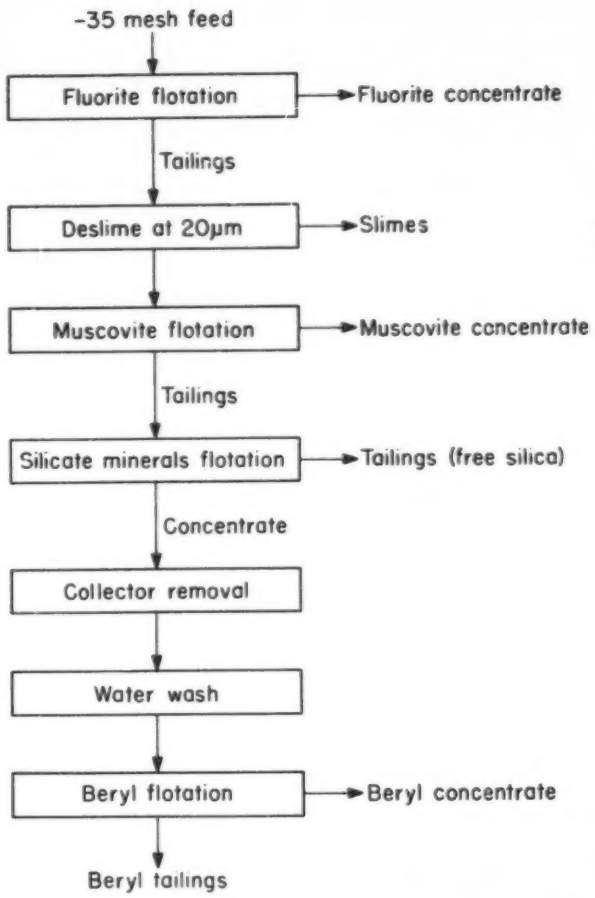

FIGURE 5. - Flowsheet for concentrating beryl from CaF_2 tailings product.

Sulfuric Acid Addition

Sulfuric acid (H_2SO_4) was used as the pH modifier and as the beryl depressant. Based on tests varying H_2SO_4 dosage from 1 to 4 lb/st, a preferred dosage of 3 lb/st was determined. In these tests, CT for both reagents was held at 3 min, and dosage for tallow amine acetate was 0.3 lb/st. As shown in figure 6, overall

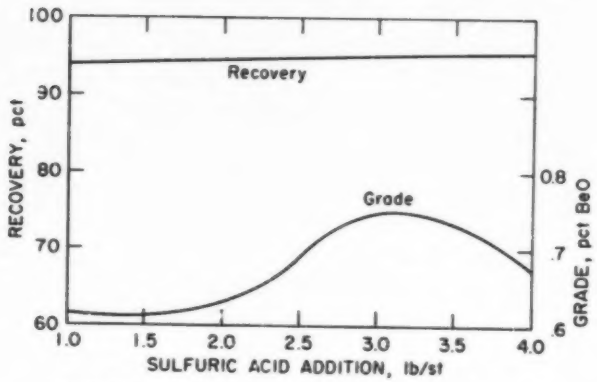

FIGURE 6. - Effect of H_2SO_4 addition on BeO recovery and grade in muscovite rougher tailings.

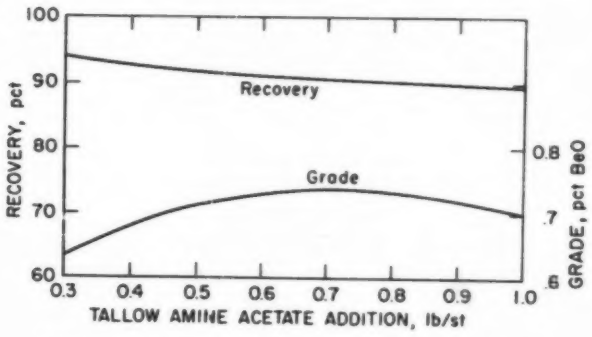

FIGURE 7. - Effect of tallow amine acetate addition on BeO recovery and grade in muscovite rougher tailings.

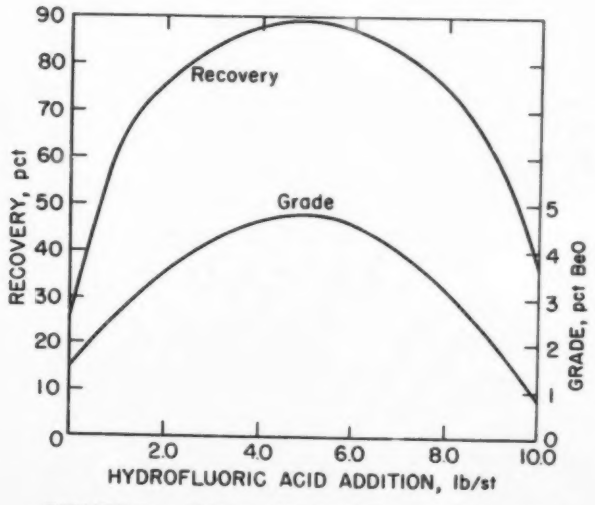

FIGURE 8. - Effect of HF addition on BeO recovery and grade in silicate rougher concentrate.

beryl recovery increased slightly with increasing H_2SO_4, while the beryl content in the muscovite tailings was highest at approximately 3 lb/st H_2SO_4. In addition, at this preferred dosage the maximum weight was removed from the muscovite concentrate, at pH 3.

Collector Addition

Based on tests varying collector (tallow amine acetate) dosage from 0.3 to 1 lb/st, a preferred dosage of 0.7 lb/st was determined. In these tests, CT was held at 3 min for both reagents, and H_2SO_4 dosage was held at 2 lb/st; pH was held at 3. As shown in figure 7, overall beryl recovery fell slightly with increasing collector dosage, while the beryl grade of the muscovite tailings was highest at 0.7 lb/st collector; at that dosage also the maximum weight was removed from the muscovite concentrate.

Silicate Removal

Direct flotation of beryl produced concentrates with grades less than 2 pct BeO; therefore, silicate flotation was used to depress the free SiO_2 and improve the grade prior to beryl flotation. Flotation testwork was performed on the silicate flotation circuit to determine the effects of (1) HF addition and (2) collector (tallow amine acetate) addition on the flotation of the silicate (beryl and feldspar) minerals.

Hydrofluoric Acid Addition

Hydrofluoric acid (HF) was used as an activator for the beryl, as a quartz depressant, and as a pH modifier. Based on tests varying HF dosage from 0 to 10 lb/st, a preferred dosage of 5 lb/st was determined. In these tests, the pulp was first conditioned with HF for 3 min, then with 1 lb/st collector for 3 min, after which the silicates were floated. As shown in figure 8, both recovery and grade increased with increased HF addition up to about 5 lb/st, then fell sharply with further HF additions; gangue flotation caused the fall in grade, while

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reagent buildup on the beryl surface lowered the recovery. At 5 lb/st HF addition, concentrate grade was 4.80 pct BeO with a recovery of 89 pct; pulp pH was 2.75 at this preferred dosage.

Collector Addition

The collector, tallow amine acetate in a 5-pct solution, was used to separate the silicate minerals from the free SiO_2. Based on tests varying collector dosage from 0 to 5 lb/st, a preferred dosage of 0.5 lb/st was determined. In these tests, the pulp was conditioned with the collector following conditioning for 3 min with 5 lb/st HF. As shown in figure 9, grade decreased steadily with increasing amounts of tallow amine acetate, whereas recovery jumped sharply with as little as 0.5 lb/st collector, then continued to increase gradually before falling off slightly at dosage levels above 3 lb/st. At 0.5 lb/st collector, concentrate grade was 4.55 pct BeO with a recovery of 81 pct.

Collector Removal

Sodium hypochlorite ($NaOCl \cdot 5H_2O$) was used to remove the collector from the mineral surfaces in order to gain selectivity in the beryl circuit. Removal of residual collector was necessary to depress gangue flotation in the beryl circuit, which would lower the beryl grade. To accomplish this, the pulp was washed for 5 min with 2 lb/st NaOCl, then allowed to settle for another 5 min. The excess liquid was decanted and the solids repulped with fresh water. Then the pulp was conditioned for 5 min and allowed to settle for another 5 min before the excess fresh water was decanted.

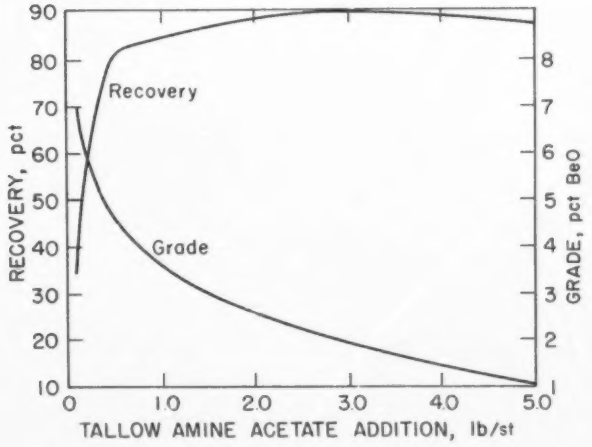

FIGURE 9. - Effect of tallow amine acetate addition on BeO recovery and grade in silicate rougher concentrate.

Beryl Flotation

Testwork had indicated that beryl selectivity could be improved by using a flotation pH of 11.0. Flotation testwork was thus performed to determine the optimum (preferred) amount of collector needed for beryl flotation at this pH.

Collector Addition

Food-grade oleic acid was used as the collector for the beryl. Based on tests varying dosage from 0.3 to 1 lb/st, a preferred dosage of 1 lb/st was determined. In these tests, pH was held constant at 11, and conditioning time at 3 min. As shown in figure 10, the beryl

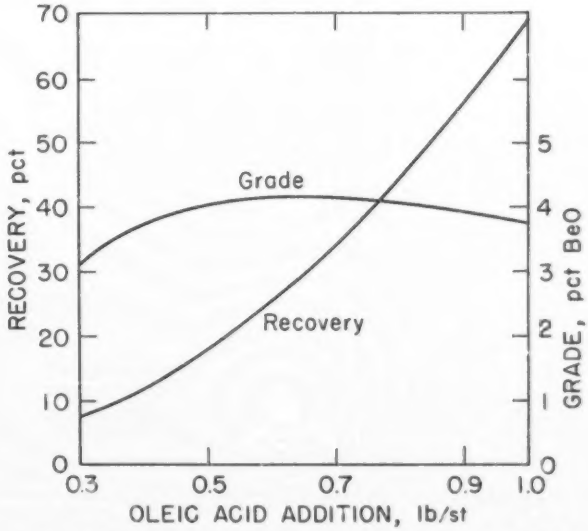

FIGURE 10. - Effect of oleic acid addition on BeO recovery and grade in beryl rougher concentrate.

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rougher grade reached a maximum of 4.15 pct BeO at 0.6 lb/st, then decreased slightly with increased additions. Recovery, however, increased steadily with increasing collector addition. Additions higher than 1 lb/st caused increased gangue flotation and thus a significant drop in grade.

Flotation Under Preferred Conditions

Under the preferred flotation conditions (table 4), a rougher beryl concentrate was produced that contained 75.3 pct of the beryl at a grade of 5.45 pct BeO. An initial cleaner concentrate contained 54 pct of the beryl at a grade of 6.11 pct BeO; after a second cleaning, recovery was 37.3 pct at a grade of 6.73 pct BeO. This is close to the minimum acceptable grade for further processing of 7 to 8 pct BeO. Flotation results are summarized in table 5.

FLUORITE-MICA SAMPLE

Fluorite Flotation

Flotation tests were performed to determine the effects of (1) collector addition and conditioning time, (2) flotation pH variation, and (3) Na_2SiO_3 addition. Three collectors were evaluated, each at a single dosage level (table 6): Pamak 4A, a mixture of 50 pct oleic acid and 50 pct linoleic acid; Aero 830, which is modified petroleum sulfonate; and food-grade oleic acid. Though recovery was slightly lower with the oleic acid, the much higher grade of 77.2 pct CaF_2 showed it to be far more selective than the other collectors. Overall, fluorite rougher concentrate grades were somewhat lower for the fluorite-mica sample than for the fluorite-beryllium sample; this was attributed to a higher slime content.

TABLE 4. - Preferred reagent dosages for byproduct recovery from fluorite-beryllium sample

Flotation stage	Reagent	Dosage, lb/st
Muscovite flotation.....	Sulfuric acid.....	3.0
	Tallow amine acetate.	.7
Silicate rougher flotation..	Hydrofluoric acid....	5.0
	Tallow amine acetate.	.5
Collector removal.....	Sodium hypochlorite..	2.0
Beryl rougher.....	Oleic acid.....	1.0

TABLE 5. - Fluorite and byproduct flotation from fluorite-beryllium sample under preferred conditions, percent

Product	Analysis		Distribution	
	CaF_2	BeO	CaF_2	BeO
CaF_2 cleaner concentrate.....	[1]98.1	<0.01	94.0	1.6
Slimes.....	3.4	.20	2.7	1.4
Muscovite concentrate.....	2.4	.12	1.5	2.2
Silicate tailings.....	.1	.02	.9	3.8
Beryl rougher concentrate.....	.8	5.45	.7	75.3
Beryl tailings.....	.4	.83	.2	15.7

[1]Sulfide, lead, and silica assays are below product specification level for acid-grade fluorite.

TABLE 6. - Rougher flotation results for fluorite-mica sample using different collectors

Reagent	Dosage, lb/st	Grade, pct CaF_2	Recovery, pct
Pamak 4A....	2.0	56.0	97.9
Aero 830....	2.0	56.4	93.6
Oleic acid..	1.5	77.2	92.2

Determination of Preferred Conditions

Oleic Acid Conditioning Time

Based on tests varying oleic acid conditioning time from 3 to 30 min, a preferred time of 10 min was determined. In these tests, conditioning time was held at 3 min for Na_2SiO_3, and dosage levels were 2 lb/st Na_2SiO_3 and 1.5 lb/st oleic acid; flotation pH was 9.0. While recovery increased steadily with increasing conditioning time (fig. 11), grade was highest at 10 min CT before falling sharply owing to increased gangue flotation.

Flotation pH Variation

Based on tests varying pH from 7 to 10.7, a preferred pH of 9.0 was determined. In these tests, CT was 3 min for both reagents, and dosage was 2 lb/st for Na_2SiO_3 and 1.5 lb/st for oleic acid. As shown in figure 12, recovery decreased very gradually until the pH reached 10, then fell very sharply, while grade continued to increase with increasing pH level. At pH 9, grade was 75 pct CaF_2 with a recovery of over 90 pct.

Sodium Silicate Addition

Na_2SiO_3 was used in the fluorite circuit as a quartz depressant. Based on tests varying dosage from 1 to 4 lb/st, a preferred dosage of 2 lb/st was determined. In these tests, oleic acid dosage was held at 1.5 lb/st, and CT was 3 min for both reagents. As shown in figure 13, both recovery and grade were highest (97.5-pct recovery at a grade of 63 pct CaF_2) with the preferred dosage.

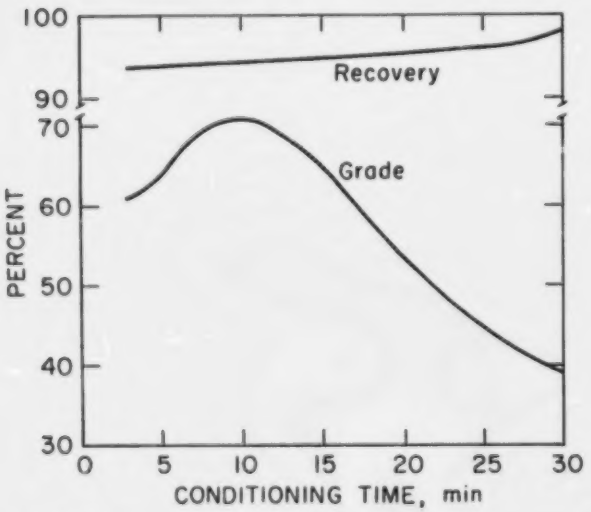

FIGURE 11. - Effect of oleic acid conditioning time on flotation of fluorite-mica sample.

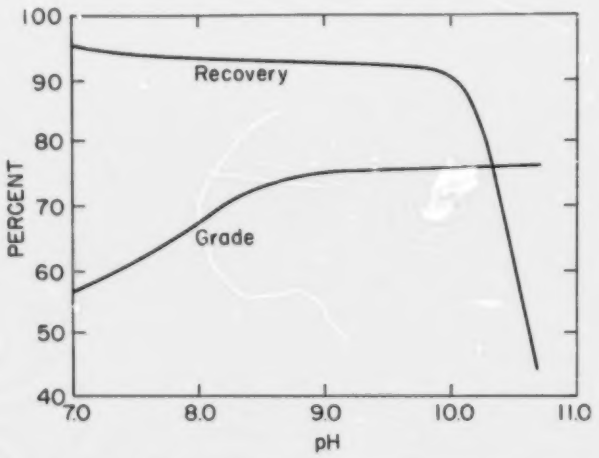

FIGURE 12. - Effect of pH variation on fluorite grade and recovery, fluorite-mica sample.

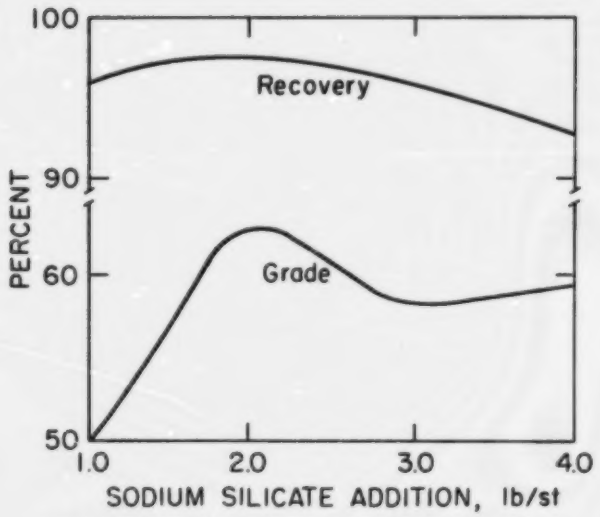

FIGURE 13. - Effect of Na_2SiO_3 addition on fluorite grade and recovery, fluorite-mica sample.

Flotation Under Preferred Conditions

Under preferred conditions--3 min CT with 2 lb/st Na_2SiO_3, 10 min CT with 1.5 lb/st oleic acid, and flotation pH of 9.0--a fluorite rougher concentrate containing 77.3 pct CaF_2 was produced with a 92.5-pct fluorite recovery. This concentrate was cleaned four times without additional reagents other than those needed to maintain the pH level; the fourth cleaner concentrate contained 96 pct CaF_2 with a recovery of 84 pct of the fluorite.

Mica Flotation

The only recoverable byproduct present in this sample was mica, which could be floated directly from the deslimed fluorite tailings. The mica in this sample was different from the muscovite found in the fluorite-beryllium sample; it contained considerable biotite and phlogopite along with muscovite. Because the mica recovery stage was not an intermediate stage, no other analytical method could be used except petrographic examination. The most effective method for treating this sample was an anionic-cationic flotation technique.

The fluorite tailings were deslimed by decantation at approximately 20 µm. Desliming was necessary in the mica flotation stage to reduce reagent consumption caused by reagents adsorbing on the slime particles. The flotation conditions for mica recovery were (1) 15-min scrubbing of the deslimed fluorite tailings with 3 lb/st NaF, (2) 15-min CT with 0.5 lb/st Na_2CO_3, (3) 3-min CT with 0.5 lb/st lead nitrate [$Pb(NO_3)_2$], (4) pH adjustment to 9.2, (5) 10-min CT with 0.5 lb/st oleic acid, and (6) 2-min CT with 0.4 lb/st Arosurf MG83A (diether amine). Under these conditions approximately 85 pct of the mica was recovered in a concentrate containing approximately 95 pct mica (table 7).

TABLE 7. - Fluorite and mica flotation from fluorite-mica sample, percent

Product	Analysis		Distribution	
	CaF_2	Mica[1]	CaF_2	Mica
CaF_2 cleaner concentrate..	[2]96.0	<1	84.0	0.5
Slimes.....	6.3	5	7.3	2.5
Mica concentrate.....	1.8	95	6.6	85.0
Mica tailings.....	1.5	15	2.1	12.0

[1]Estimated by petrography.

[2]Silica value was below product specification level for ceramic-grade fluorite.

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CONCLUSIONS

Experimental results showed that fluorite readily floated from the fluorite-beryllium sample using oleic acid at pH 9.0. Bench-scale flotation using 3 lb/st Na_2CO_3, 3 lb/st Na_2SiO_3, and 2 lb/st oleic acid recovered 94 pct of the fluorite in an acid-grade recleaner concentrate, which contained 98.1 pct CaF_2. A muscovite concentrate was obtained from the deslimed fluorite tailings using 3.0 lb/st H_2SO_4 and 0.7 lb/st tallow amine acetate. The silicate minerals were floated from the free silica using 5 lb/st HF and 0.5 lb/st tallow amine acetate. The silicate tailings product contained 99 pct SiO_2 with a recovery of 90 pct. A beryl concentrate was produced containing 75.3 pct of the beryl with a grade of 5.45 pct BeO.

Experimental results showed that fluorite can be floated from the fluorite-mica sample using oleic acid at pH 9.0. Flotation using 2 lb/st Na_2SiO_3 and 1.5 lb/st oleic acid produced a ceramic-grade recleaner concentrate containing 96 pct CaF_2 at a recovery of 84 pct. A mica concentrate containing 95 pct mica at 85 pct recovery was obtained from deslimed fluorite tailings using 3 lb/st NaF, 0.5 lb/st Na_2CO_3, 0.5 lb/st $Pb(NO_3)_2$, 0.5 lb/st oleic acid, and 0.4 lb/st diether amine.

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